SCIENCE REQUIREMENTS DOCUMENT

Binary Critical Aggregation Test – 5 (BCAT-5)

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Science Requirements Document (SRD)
Binary Critical Aggregation Test – 5
(BCAT-5)

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SCIENCE REQUIREMENTS DOCUMENT

Binary Critical Aggregation Test – 5 (BCAT-5)

This is an updated signature page to reflect the change in BCAT-5 Sample 9 and the corresponding changes that propagate throughout the BCAT-5 Science Requirements Document (SRD). Sample 9 was previously named "BCAT-5 Sample 9, Aspheres", and since its replacement, this sample has had its name changed to "BCAT-5 Sample 9, SeededGrowth". It is still from Paul Chaikin and Andrew Hollingsworth at NYU. And the Aspheres sample may yet be flown in BCAT-6 (which has yet to be officially manifested) using a new compatible solvent. The Aspheres sample was replaced with the SeededGrowth sample when the Viton® containment seals of the BCAT sample module and the Viton® septum of the Aspheres sample cell were found to be incompatible with the DMSO solvent of the Aspheres sample. The SeededGrowth sample materials have been qualified and flown in the BCAT-4 flight experiment using a different concentration of seed particles.

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BCAT-5 SRD version.1.0.6, updated December 2 2008

1. Executive Summary

1.1. Description of Experiment

The goals of this International Space Station (ISS) bench top and/or ceiling rail-mounted experiment are twofold: (1) to further investigate fundamental science problems in colloidal science, (2) and to evolve the field of 'colloidal engineering', which creates materials with novel properties using colloidal particles as precursors. In both cases, gravity-driven sedimentation, convection, and jamming preclude these experiments from being carried out on earth; a microgravity environment is required to attain these goals.

BCAT-5 will study 10 colloidal samples that can be grouped into four classes:

Samples 1 – 5 (PhaseSep) will study collapse (phase separation rates that impact product shelf-life). In microgravity the physics of collapse is not masked by being reduced to a simple top and bottom phase as it is on earth.

Samples 6 – 8 (Compete) will study the competition between phase separation and crystallization, which is important in the manufacture of plastics and other materials.

Sample 9 (SeededGrowth) will experimentally study the properties of concentrated systems of small particles in an index matching fluid when the particles are all monodisperse 'hard spheres', except about 0.2% of them that are ~11.5 times larger in diameter and which may induce crystallization by heterogeneous nucleation..   The theoretical prediction is that the use of the right size and concentration of seed particles ('nano-dirt') can be used as a way to control the size of crystallites by reducing the free-energy barrier associated with crystal nucleation.

Sample 10 (3DMelt) will look at the mechanisms of melting using 3-dimensional temperature sensitive colloidal crystals composted of particles that change size with temperature. The International Space Station (ISS) cabin temperature changes a few degrees during a two week period.

This experiment is envisioned as a direct follow-on to the Binary Colloid Alloy Test 3 (BCAT-3) and Binary Colloid Alloy Test 4 (BCAT-4) experiments, which themselves are follow-on experiments to previous flight experiments, including: the Physics of Colloids in Space (PCS), earlier iterations of the Binary Colloid Alloy Test (BCAT, BCAT-2), Colloidal Gelation (CGel), and the Colloidal Disorder Order Transition (CDOT) experiment. The BCAT-5 experiment is intended to both provide science results and optimize sample selection for future Light Microscopy Module-Colloids (LMM-Colloids) and Solution Crystallization Diagnostics Facility (SCDF) experiments.   The LMM-Colloids and SCDF experiments will involve many of the BCAT-5 Principal Investigators (PIs) and international collaborators, and they are currently scheduled to fly aboard the ISS starting around 2011-14.

Our first two sets of samples are made from mixtures of colloids and polymers which undergo a variety of phase transitions. The third set consists of colloidal particles with

effective volume fractions resulting in an amorphous or glassy phase in normal gravity. Earlier experiments (CDOT-1 & CDOT-2) have observed that gravity plays an overwhelmingly important role on the crystallization and glass-formation behavior of spherical colloids. We intend to explore this in a new system of colloids in which we adjust the shape.

For all samples, we will begin each experiment by mixing the sample, and then allowing its structure to evolve with time. The time evolution of the structure will be recorded using a camera controlled by the EarthKAM scripting software. Although simple in setup and execution, BCAT-5 has the unique ability to provide important data on experimental systems that cannot be accessed on earth and, like its predecessor flight experiments, to contribute to our fundamental understanding of the thermodynamics and kinetics of colloids, in particular, and materials in general.

1.2. Scientific Knowledge to be Gained

When the masking effects of gravity are removed, the rate at which the BCAT-3 critical point samples separated into two phases showed an unexpected behavior. This result was in direct contrast to the normally observed phase separation seen on earth where important components sediment during the measurements. The BCAT-5 experiments are essential to the understanding of the origin of this, and for providing quantitative data for theorists to model. In addition BCAT-5 extends the range of behavior beyond exploration of the critical point to the region in which samples separate into gas, liquid and crystalline phases simultaneously. Because BCAT-5 will follow the evolution of samples for days to weeks (and even months since the samples will continue to evolve, even in storage) in the microgravity environment, there is simply no other way to gain this important class of data.

BCAT-3 was the first experiment to use the size advantages of colloids, which can be used as model atoms, to systematically and precisely locate the critical point and characterize the behavior around it. These particles are not only large enough to scatter light (and thus be visible to the camera, as well as the naked eye), but also large enough to slow down the dynamics to speeds that allow us to photograph the phase separation of samples over a period of weeks, assisted by apparatus already onboard the ISS.

Moreover, increased knowledge of some of the areas of this basic physical research may have future benefits in the application of the same physical processes on earth. Supercritical fluids (fluids possessing properties of a gas and a liquid simultaneously) have numerous applications in a wide variety of fields. An example is supercritical carbon dioxide, which represents a solvent that can perform a wide variety of extraction and processing duties, an environmentally friendly solution replacing noxious solvents used in dry cleaning, decaffeination of coffee beans, and extraction of delicate pharmacological molecules from plants for use in new drugs. The development and use of newer supercritical fluids is dependent on further understanding of the critical points of those fluids, which the BCAT experiments are providing. In addition, the specific dynamics of these colloid-polymer mixtures are of great economic importance to product

stability: if phase separation occurs during the shelf-life of certain household products, then their value to the consumer precipitates. There is thus a significant commercial incentive, in a market worth billions of dollars annually, in coming to a better fundamental understanding of this particular system, and BCAT-5 will certainly aid in that process.

The so-called 'model hard-sphere' particle suspension experiments (samples 9–10) will extend our understanding of known self-assembly and thermodynamics processes in complex fluids. Clean observations of phase transitions in a microgravity environment will provide much needed insight into the interplay of particle concentration, seeding, and size with sedimentation in affecting phase behavior. These effects are normally masked in experiments on earth. Traditional questions about the relative packing fractions, which crystallization phase is manifested, and the passing from one phase to the other, can be studied in these systems with exquisite resolution without the perturbing effects of sedimentation and gravitational jamming.

1.3.   Value of Knowledge to Scientific Field

Because the BCAT-3 and BCAT-4 experiments have forced us to question the applicability of existing molecular theory for critical phenomena to colloid-polymer mixtures, five of these ten samples (samples 1–5) will be critical point (phase separation) samples. All of the BCAT-3 samples fell along a straight line in the phase diagram, and BCAT-5 will allow us to probe surrounding points, allowing a far more precise location of the critical point (which has never been carefully located in these systems), and will provide the quantitative data needed by theorists to confirm new models of what is happening.

Samples 6-8 will probe a somewhat different phenomena: three-phase separation kinetics. This regime remains virtually uncharacterized in any type of material including molecular fluids or complex mixtures. BCAT-5 takes advantage of a substantial opportunity to fill a gap in the knowledge of these statistical processes. By examining the kinetics in three samples of different composition, we intend to show that significant quantitative differences in kinetics occur even though the resulting phases are similar.

Samples 9 – 10 are of a different class. They will consist of colloidal particles whose size and concentration (and the existence of seed particles in the case of Sample 9) are tuned to either suppress crystallization or increase the rate at which crystals nucleate using spherical particles (for Samples 9 and 10. The results of this experiment have important consequences for the control of the resulting crystal size distribution. BCAT-5 represents a significant opportunity to explore the fundamental physics behind these processes by crystallizing in microgravity where there is no gravitational jamming to suppress the natural ordering process observed earlier in microgravity.

1.4. Justification of the Need for a Space Environment

Both critical point and crystal samples are dramatically affected by gravity. In BCAT-3, we observed the formation of a bicontinuous network in microgravity that coarsened over time until complete phase separation was achieved. On earth (in 1-g), by the time significant phase separation has begun, all of the particles have settled to the bottom of the sample chamber. Consequently, bicontinuous networks never form on earth.

Similarly, the formation of colloidal crystals is strongly affected by sedimentation; this has most graphically been demonstrated with the aid of microgravity by the results of the early experiments of Chaikin and Russel, who showed that the morphology of colloidal crystals grown in space is completely different from that grown on earth. The primary reason for this is sedimentation: as the crystals sediment, the shear of the fluid flowing past their edges is sufficient to destroy them. In addition, the sedimentation time of the crystals rapidly begins to compete with the diffusion time of the accreting particles, significantly changing the growth mechanism.

The effects of sedimentation and jamming can be mitigated to a certain degree on the ground, by changing the index matching solvents (needed to avoid multiple scattering and particle interactions) to a nearly buoyancy-matched combination. However, these heavy organic solvents invariably swell the colloidal particles, which then selectively absorb the heavier solvent and gain density. It is therefore impossible on the ground to conduct an experiment where the particles remain buoyant for the weeks and months it takes to observe the processes we have already seen in BCAT-3 and earlier crystallization experiments. By the time these processes have occurred, the particles in density-matched solvents have changed their density slightly and settled to the bottom of the sample chamber. The microgravity environment is therefore absolutely crucial to our ability to conduct these experiments and investigate these fundamental physical processes.

2. Background

2.1. General Description of the Scientific Field

The conceptual motivations for this work are coupled to current research in complex fluids, optics, and many-body statistical physics. The bulk of this research centers on the physics of complex fluids, an important subfield of condensed matter physics. Complex fluids are soft materials such as colloidal suspensions, emulsions, polymer solutions, membranes, and mixtures thereof, whose structure and dynamics are strongly influenced by entropy and by relatively weak mechanical forces. They are thus particularly well suited for the microgravity environment of the ISS where the main mechanical force, gravity, is severely reduced. These experiments will focus on mixtures of colloidal particles and other soft materials. These materials are intriguing from both fundamental and practical points of view.

Research on these substances is also driven by a variety of practical applications ranging from the prospect of using these materials as templates for photonic materials and lithography, to their uses in ceramics and as biochemical sensors. In a different vein, studies of complex fluids are increasingly stimulated by analogies from cell biology, and in some cases provide critical insights about mechanisms that arise in the crowded, aqueous, and near-room-temperature cellular environments. In still other systems, particle additives offer practical control of fluid rheologies, thus improving the performance of conventional materials such as paints, motor oils, food and cosmetics.

During the past several years we have gained a great deal of versatility and experience in the production, characterization and control of novel colloidal particles. Simultaneously we have developed processes and experimental techniques which open new fields of research using these particles. We can now produce via photolithography particles of arbitrary two dimensional shape and through emulsion chemistry a wide variety of particle shapes in three dimensions, suitable for thermodynamic, hydrodynamic and nonlinear studies and processing. We plan to explore the fundamental problems of how densely different shaped particles pack, e.g. whether ellipsoids, tetrahedra, etc. pack denser randomly or in a crystalline array. This addresses an age-old problem of the geometry dependence of glasses and crystals. We also expect our non spherical particles will lead to the discovery of new liquid crystalline phases and in general to new condensed phases of matter. Aside from the fundamental knowledge gained from such studies they will also pave the way for techniques to fabricate complex micro and nanoscale building blocks and to self-assemble them into devices.

The colloidal architecture being developed needs a microgravity environment to manipulate and control particles (on the micron scale) made of different materials which would otherwise sediment and separate. Once the processes are understood they can be applied to nanoscale particles for use on earth. Such nano-particle will not sediment, but can only be processed according to rules established at the larger lengths scales where we can observe the particle interactions. Thus we plan to develop a technology in micro-g on micron particles to be used on earth on nanometer particles.

In BCAT-5, we focus on colloidal suspensions, which exhibit a rich and varied range of properties. They are of great scientific interest, as well as of great practical importance. They can be synthesized with exquisite precision and control, and can be formed from a wide range of materials. Colloidal particle distributions can be made highly monodisperse. The interactions between the particles can also be finely tuned, and can vary from repulsive to attractive, over a controllable range. The particles can be induced to self-assemble into a wide range of structures, many of which have long-range order. They can serve as model systems for the study of fluid and solid properties, with the colloidal particles playing the role of thermodynamically-driven atoms or molecules. The relaxation times that characterize their behavior are much longer than those of atomic or molecular materials, making them much more accessible to experimental probes on the benchtop scale. In addition, the larger size of the colloidal particles facilitates the study of the structure and dynamics of the suspensions, allowing, for example, the use of optical techniques such as static and dynamic light scattering and laser crystallography, or Bragg scattering.

Understanding critical phenomena was an important theoretical advance in physics during the last half century, but ground-based experiments have been limited by gravity. A gravitational field invariably causes a denser liquid phase to fall to the bottom of any container, preventing direct observation of the spatial structure of phase separation over the long term. In the absence of gravity, however, we can watch the boundary between separating phases and it does not look at all the same as on earth. The microgravity environment allows the phase boundary to assume its true thermodynamically-driven shape.

Colloidal suspensions exhibit a wide range of structures, both ordered and disordered, with correlations that often extend to the size of the system. Furthermore they exhibit a wide range of dynamics, which can often be tied closely to the structure of the system. Their rich phenomenology derives from a fascinating interplay of physical, chemical and hydrodynamic mechanisms whose realization provides a unique opportunity for the study of statistical mechanics in classical many-body systems. Recent experimental and theoretical progress relevant to the present includes studies of the role of entropy and interparticle interaction in affecting self-assembly and directed assembly in systems of monodisperse hard-spheres, particle suspensions with added particles or polymers, monodisperse emulsions with added polymer, binary emulsions, suspensions of rod-like particles in mixtures of spheres, liquid crystal emulsions, and charged-stabilized particle suspensions.

The high degree of control over the synthesis of colloidal particles and our ability to finely tune the interaction between them also makes it possible to use colloidal particles as precursors for forming new materials; these should have unique and novel properties. This new route to materials synthesis has come to be called 'colloidal engineering', allow the formation of materials with unique and fascinating properties. For example, these alloys may form the precursors for very high quality ceramics. Alternatively, one set of particles could be plastic and the other set of particles could be a metal or a semiconductor. After formation of the binary superlattice, sintering at a temperature above the glass transition of the plastic could provide a plastic sheet containing the other particles in ordered arrays. Such a material should have unique optical, or even electronic, properties. For example, this may be a simple method for fabricating an array of quantum dots that has useful optoelectronic properties. Alternatively, colloidal engineering may provide a simple route to the synthesis of photonic band gap materials [6, 7], or structures that have a greatly reduced phase space available for radiation [8].

Current routes for fabricating photonic band gap materials in the optical regime rely on three-dimensional lithography, which is a very challenging and difficult process. Colloidal engineering may offer a simple method for making these materials that completely bypasses many of these difficulties. These superlattices could also be used as novel optical switches or displays. For example, instead of using solid colloidal particles, monodisperse emulsion droplets or colloids filled with liquid crystal molecules could be used to form the structures, allowing their optical properties to be switched by application of an external electric field. The switching voltage is a function of the particles size, making it feasible to switch a Bragg scattering matrix on and off by manipulating only the large droplets in a superlattice, thus making the smaller one Bragg scatter. This

technique could form the basis for a novel optoelectronic display technology that not only switches light, but also controls the direction or color of the displayed light. Many other novel materials can be envisioned.

2.2.   Proposed Experiments

The results from BCAT-5 will greatly enhance our knowledge of phase separation (critical phenomena) for an important class of complex fluids. Moreover, some of these samples will indicate how concentration at high number density (along with particle seeding in the case of the SeededGrowth sample) effects crystallization in microgravity. Additionally, the science results that are returned by this work will impact future experiments with colloids, and possibly those being done in microgravity, where the masking effects of sedimentation, convection, and particle jamming are removed.

BCAT-5 has four parts, BCAT-5-PhaseSep, BCAT-5-Compete, BCAT-5-Aspheres, and BCAT-5-3DMelt:

2.2.1.   *BCAT-5 Phase Separation (PhaseSep)*

For the PhaseSep Samples (1 – 5), astronauts photograph samples of polymer and colloidal particles (tiny submicron size spheres suspended in liquid) that model liquid/gas phase changes. These samples are initially homogenized (randomized) and then left to evolve (self-organize). Results will allow scientists to see some of the fundamental physics concepts that are behind product collapse; these observations have been cloaked by the effects of gravity. The BCAT-5-PhaseSep samples will be formulated using key components found in products like Downy®. Many such products require expensive additives to ensure that collapse does not occur during the stated shelf-life. A fundamental understanding of the underlying physics that is needed to stabilize these everyday products may enable a formulation with enhanced performance and stability, while simultaneously lowering the cost of manufacture. (Lynch, Weitz, and Lu)

2.2.2.   *BCAT-5-Compete*

For the Compete Samples (6 – 8), the focus will be specifically on the effect of phase separation on crystal growth. On Earth, gravity causes the colloids to settle, making such a study particularly difficult. Performing these experiments in the microgravity environment of the International Space Station will allow scientists to study growth of much larger structures, and, thus, maximize the extent to which the behavior can be explored. Improved understanding of these processes will lead to more refined manufacturing processes and commercial products. The competition between a phase separation process and an order-disorder transition remains largely unstudied and offers an opportunity to observe some fascinating behavior. The overarching goal of all these experiments is to develop the key knowledge to help make colloidal engineering a reality. In addition, this

experiment should help scientists understand the fundamental properties of colloid-polymer mixtures to further improve the commercial use of such systems. (Frisken and Bailey)

2.2.3.   *BCAT-5-SeededGrowth*

For the SeededGrowth Sample (9), plans are to experimentally explore the theoretical prediction [1] that the use of seed particles can be used as a way to control the size of crystallites. The control of crystallite size is important in many industrial processes. By introducing the the right size and concentration of 'nano-dirt', we use this experiment to record the effect of large (10x) spherical seed particles on crystallization. "Small nuclei grow on the seed [and] as they grow, the presence of a [larger] curved substrate makes it difficult to maintain an unstrained structure. At some stage, the precritical nuclei break away from the surface, and the critical nucleus is only formed in the bulk [1]." The seed particles are identical to the smaller PMMA spheres, including the thin polymeric steric layer attached to the particle surfaces.

[1] A. Cacciuto, S. Auer, D. Frenkel, "Onset of heterogeneous crystal nucleation in colloidal suspensions", Nature, 25 March 2004, Vol. 428, pp. 404-406.

In the microgravity environment aboard the International Space Station, questions about homogeneous and heterogeneous crystallization will be probed without the perturbing effects of sedimentation and gravitational jamming. (Chaikin and Hollingsworth)

2.2.4.   *BCAT-5-3DMelt*

For the 3DMelt Sample (10), scientists are planning a microgravity experiment that takes advantage of temperature-sensitive polymers and microgel particles to tune soft matter through melting and crystallization transitions. This approach recently enabled them to identify premelting phenomena at grain boundaries in bulk colloidal crystals (2005 Science Cover Article). The 3DMelt experiment will utilize similar thermo-sensitive particles. The International Space Station (ISS) cabin temperature changes a few degrees during a two-week period. These temperatures will be recorded. Concurrent changes in particle size and sample volume fraction should cause the sample to move in and out of the crystalline regime. We will record these changes using a camera. This limited experiment will enable us to explore the feasibility of long term experiments on-board the ISS using these materials. (Yodh)

Astronauts on board the International Space Station (ISS) set up the BCAT-5 experiment and use a camera to take pictures of all of the above samples right after they have been homogenized and as they evolve in time. This is done both manually and with an ISS

computer program called EarthKAM. They also use a small flashlight and a camera to capture pictures of the colored light diffracted by crystals that may form for some of the samples (6 – 10) in the absence of gravity but not on Earth.

Detailed Research Description:

BCAT-5 Phase Separation (PhaseSep), Samples (1 – 5):

Fabric enhancers are composed of mixtures of vesicle and polymers which, in some cases, form weak particle gels. These gels often coarsen exhibiting sintering, cracking or collapse, which significantly reduce the product shelf life. The factors that contribute to coarsening are enigmatic, as the processes are often concealed by the gravitational compression of the gel. Microgravity experiments offer a unique opportunity to elucidate coarsening mechanisms in these weak gel systems.

BCAT-5-Compete, Samples (6 – 8):

The BCAT-5 Compete samples consist of colloids suspended in solvent with added polymer. As with some of the other BCAT-5 samples, such as the PhaseSep samples, the polymer causes an attractive interaction between the colloids. By changing the amount of colloid and the relative amount of colloid and polymer, the equilibrium state of the sample can be changed. The Compete samples will have equilibrium concentrations that result in coexistence of colloidal liquid, colloidal gas and colloidal crystal phases. The purpose of these experiments is to study the kinetics that lead to these unique coexistences.

The samples will be homogenized by mixing and then allowed to evolve in time. They are expected to take several days to reach a near equilibrium state. During this time the EarthKAM system will be used to take high-resolution photographs of the samples at regular intervals. As the phase separation / crystallization kinetics begin immediately after the samples are mixed, the interval between images should be relatively short. As the kinetics proceed, the time between images can be increased. Imaging such as this has been and will be performed during BCAT-3 and BCAT-4. The down-linked images will be analyzed using standard techniques to measure the spatial size of concentration variations in the sample or sizes of crystallites as a function of time.

Because crystals should be present, the Compete samples will likely require use of a small flashlight to determine optimal lighting followed by a repeat of the EarthKAM system measurements in an effort to extract as much data as possible regarding the time dependence of crystallite formation.

Ultimately the experiment is designed to determine if, in samples which both phase separate and crystallize, the dynamics of either process is affected by the other. For example, one possible scenario might be that phase separation, which induces local density increases, reduces the initiation time for crystallization because of the increased

density. These systems are relatively unexamined and a wealth of new phenomena may be observed.

BCAT-5-SeededGrowth, Sample 9:
A good deal of the behavior of these systems is governed by their entropy. This is related to the presence of seed particles. The driving force toward ordering, while small, may be enhanced and the system may present a unique way to study glassy dynamics in a "monodisperse" suspension when seed particles are present. This sample may help us understand how to control the size of crystals and why monodisperse samples that are glass-like on earth crystallize in microgravity.

BCAT-5-3DMelt, Sample 10:
We will first prepare a monodisperse nearly-hard-sphere colloidal suspension near its crystallization point. Then small temperature changes that decrease particle volume fraction will move the equilibrium system towards and away from the melting transition. Briefly, the key ingredient in these samples is thermosensitive polymer, i.e. NIPA polymer (poly(N-isopropylacrylamide)). The temperature-sensitive character of the samples stems from the temperature dependent solubility of NIPA polymer in water. Below its Θ temperature of ~31°C, water is a good solvent and NIPA polymer assumes a swollen coil form; in this regime a small increase of temperature increases monomer-monomer attractions and thus the size of the isolated polymer decreases. Above the Θ temperature, water is a poor solvent and NIPA has a collapsed globule form. Similar ideas apply to NIPA-based microgel particles. For example, we have synthesized 'soft-repulsive' particles made from cross-linked NIPA polymer, whose diameter and volume fraction can be tuned by temperature. Depending on ground-based research progress we will use NIPA microgel particles or core-shell PS-NIPA and silica-NIPA particles. This proof-of-principle experiment will simply record sample temperature and observe (by photography) whether the samples crystallize and at what temperatures the samples experience the fluid-solid transition. This information will be useful for future experiments planned for ISS. If the photographic images are of sufficient quality, it should also be possible to assess the morphology of the crystal (*e.g.* is growth dendritic) and the dynamical motions of the sample in its co-existence region.

2.3. Current Research in Support of Proposed Experiments

Much of the current research effort is associated with the preparations for the flight experiments. In addition, more data analysis is being carried out for the flights that have already taken place, primarily to attempt to learn as much as possible from the photographs, through the use of improved digital image processing.

Concurrently, the near buoyancy match significantly extends the amount of ground-based preparatory research that can be done. Current work at Harvard University is exploring the dynamics of gels, which appear to be driven by the same phase separation processes that occur near the critical point. However, by moving far away from that point in the phase diagram, we reach a regime where the rate of phase separation is far faster, so that the near buoyancy-matched samples can be imaged in the time frame where the particles

still remain buoyant (days on the ground, not months as in microgravity). Moreover, we have also observed cluster phases on the ground, and current work is seeking to find out if, in fact, these clusters are created by the same processes that create freely-circulating clusters in the microgravity environment of the ISS.

At Simon Fraser University, concurrent experiments will study the start of the phase separation kinetics. The early stages of these processes are less affected by gravity. In addition measurements of the simultaneous nucleation of crystals will provide a useful reference relative to the microgravity studies.

Research is being carried out to learn how to synthesize new particles. At NYU, Hollingsworth is developing the synthesis routes required to make aspherical particles. New methods are being developed that require the use of much smaller quantities, making it feasible to synthesize the required material in the necessary volumes.

2.4.   Anticipated Advance in the State of the Art

Addressing the questions proposed above would significantly increase our understanding of the properties and behavior of colloidal suspensions. In particular, BCAT-3 has approached phase boundaries near the critical point for these model colloidal systems to a much closer degree than any others, primarily because the microgravity environment allows observations for the far longer time scales that occur near the critical point. The hard-sphere particle crystallization experiments will provide crucial guidance in the use of colloidal precursors for materials synthesis, and would help establish colloidal engineering as a new synthesis route.

3. Justification for Conducting the Experiment in Space

3.1.   Limitations of Ground-Based Testing

The primary limitation with ground-based work results from sedimentation. A second less critical problem arises due to convection effects, which are also gravity induced. Both of these effects will be greatly reduced in microgravity. A basic understanding of the limitations imposed by gravity comes from the problems encountered in current experiments. We review these first, and then discuss more detailed estimates of the effects of gravity, even in the optimum case.

Experiments at the University of Edinburgh have probed the formation and structure of crystals from monodisperse colloidal particles using microscopy. Small capillary tubes (~2 mm wide x 100 μm thick) were used as sample cells. The samples were loaded in a fluid state, the cell was sealed and the measurements begun. In the course of about an hour, the samples crystallized. The crystallization process was studied and the final structures were determined by imaging. However, during the course of the experiment, it was inevitably noticed that the particles sediment, so that the top of the cell has a lower density, which typically remains fluid, while the bottom has a higher density, where the crystals form. Thus, it is impossible to accurately set the volume fraction. Moreover, the

sample at the bottom is always under the additional osmotic pressure of the sample above and this result has a direct effect on the sample properties. As shown by the results of the CDOT experiment, the morphology of the crystals is significantly modified by gravity-induced settling. This behavior limits the size of the crystals that grow, which will place a significant limitation on their use for materials growth.

Experiments conducted by Segrè at Penn and at Harvard also highlight the effects of gravity. He used time lapse video to record the formation and growth of the crystals from larger scale samples, again of monodisperse particles. He first used the standard mixture of index-matching fluids, tetralin and decalin, for which there is a density mismatch of $\Delta\rho \approx 0.25\,\mathrm{g/cm^3}$. Thus the colloidal crystals observed tended to sediment rapidly. He then repeated the experiment using cycloheptyl bromide, which can be used to achieve a more nearly buoyancy matched sample while still index matching the PMMA particles. He estimated that the density mismatch was decreased by about two orders of magnitude, to $\Delta\rho \approx 0.002\,\mathrm{g/cm^3}$. This is probably an optimistic estimate, with the actual density match being poorer; however, while the sedimentation velocity was reduced, and the crystals were larger and more dendritic, they also clearly continued to sediment. Because of uncertainties in mixing volumes, it is unlikely that density matching closer than this can be achieved on earth; differences in thermal expansions also limit the exact buoyancy match. In addition, the only way to reliably and accurately set the volume fraction of the samples is to take advantage of their phase behavior. Their volume fraction, ϕ, can be adjusted to be in the two-phase region, with $0.50 \leq \phi \leq 0.55$, where both the fluid and crystal coexist. The fluid has a volume fraction equal approximately to this lower bound, while the solid corresponds to the larger volume fraction. By allowing the denser crystals to sediment to the bottom of the sample, the volume fraction of the supernatant fluid is set at $\phi = 0.5$. Accurate adjustment of the volume fraction is essential for all experiments, and this procedure has proven to be the most reliable and accurate method. Thus, even the slow sedimentation of the near-density matched samples is highly desirable.

A final observation about gravity induced effects comes from some of the results obtained in the CGel glovebox experiment. In this experiment, samples remained in microgravity for about four months at which time they were photographed. Although the results are not very quantitative (no light scattering was performed), some of the pictures seem to show a noticeable difference in apparent photographic density from the top to the bottom of the cell. One explanation for this observation is that the material had sedimented slightly during the course of the experiment. Thus, it may actually be desirable to use as close to buoyancy matched particles as are available in the microgravity experiments to minimize this effect for the most delicate of samples and the longest duration experiments.

We can make several estimates of the effects of gravity on the crystals. The first one is to calculate when sedimentation can compete with diffusion for the growth of the crystals. The concept here is that a free crystal grows by diffusion of the accreting particles to the surface. Competing with this is the sedimentation of the whole crystal. We can estimate an effective Peclet number, Pe_{eff}, which expresses the ratio of the time for a single particle to diffuse its own size, t_D, to the time for the crystal to sediment a single particle

size, t_C. We might expect that when $Pe_{eff} = t_D/t_C \sim 1$, the effects of sedimentation will become significant. This will allow us to estimate a maximum crystal size that can be achieved. We do this for crystals from monodisperse particles as all the required parameters are known for them.

The buoyant mass of a crystal of typical radius R_C is given by

$$m_b = 8 \Delta \rho_p \Delta \rho R_c^3 \qquad (1)$$

where $\Delta \rho_p = 0.05 \, \text{g/cm}^3$ is the difference in particle density between the crystal and the fluid, while $\Delta \rho$ is the intrinsic difference in density between the particles and the surrounding fluid. The sedimentation velocity can then be calculated by balancing the gravitational force on the crystal with the Stokes drag of the fluid, resulting in

$$v_C = \frac{\Delta \rho_p \Delta \rho \, g \, R_C^2}{6 \pi \eta} \qquad (2)$$

where g is the gravitational acceleration constant and η is the viscosity of the surrounding fluid, which we take to be the value of the viscosity of the fluid phase which is about 50 times that of the solvent. The characteristic times are then

$$t_C = \frac{R}{v_C} \text{ and } t_D = \frac{R^2}{D},$$

where D is the diffusion coefficient of the single particles. This value can be calculated using the Stokes-Einstein relation,

$$D = \frac{k_B T}{6 \pi \eta R} \qquad (3)$$

where T is the absolute temperature and k_B is Boltzmann's constant. It follows that the effective Peclet number for this form of crystal growth is,

$$Pe_{eff} = \frac{8 \Delta \rho_p \Delta \rho R_C^2 R^2 g}{k_B T}. \qquad (4)$$

If we use $Pe_{eff} = 1$ as a criterion for when sedimentation becomes important, we can determine the maximum crystal size that can grow under different conditions,

$$R_{C,max} = \sqrt{\frac{k_B T}{8 \Delta \rho_p \Delta \rho g R^2}} \approx \frac{3 \times 10^{-7}}{R \sqrt{\Delta \rho g}} \text{ cm} \qquad (5)$$

using CGS units. If we use $R = 0.5 \, \mu\text{m}$, we can calculate the size of PMMA crystals that can be formed on earth with the standard index matching solvents, decalin and tetralin,

for which $\Delta\rho \approx 0.25\,\mathrm{g/cm^3}$ and $g \approx 10^3\,\mathrm{cm/s^2}$. Substituting the appropriate values into Eq. (5), we obtain a value of $R_{C,max} \sim 4\,\mu m$. This result is consistent with the observation that dendritic crystals are never observed on earth. The value of $R_{C,max}$ varies inversely as the square root of both g and $\Delta\rho$, allowing us to estimate the effects of both buoyancy matching in microgravity. If we improve the buoyancy match by two orders of magnitude, the size of the crystals will increase by one order of magnitude to $R_{C,max} \sim 40\,\mu m$. By comparison, using the standard non-buoyancy matched fluids, but doing the experiment in microgravity increases the maximum crystal size three orders to about $R_{C,max} \sim 4\,mm$, again consistent with what was observed in the CDOT experiments. Combining the approaches of near buoyancy matching and microgravity could produce crystals of remarkable sizes, $R_{C,max} \sim 4\,cm$!

Of course, these are the simplest cases to consider. The key is the square root dependence on both $\Delta\rho$ and g. Thus even a far less favorable density mismatch of 20 would decrease the size of the crystals by a factor of 10, while microgravity would still provide the benefit of a factor of 10^3. As a result, we might estimate $R_{C,max} \sim 400\,\mu m$ in the most unfavorable case of binary alloys with a large density mismatch, provided we do the experiment in microgravity. This size is still quite reasonable for making materials with interesting optical properties.

Finally, it also interesting to estimate the actual sedimentation velocity for some cases. Using Eq. (2), and assuming a 100 μm crystal of PMMA in decalin and tetralin in microgravity, $v_C \sim 0.5\,\mu m/sec$ on earth, where we have assumed that $\eta = 1$ Poise. In microgravity, this is reduced by 10^6, becoming more like about $v_C \sim 1\,\mu m/month$.

In evaluating the significance of these calculations, we feel that the estimates for the monodisperse PMMA crystals are probably more relevant to the glassy PMMA and colloid-polymer mixtures.

3.2.   Limitations of Drop Towers

The length of time required for the formation of any of these structures is far too long for short-term microgravity experiments, such as those performed in a drop tower. In this arrangement, low gravity is achieved only for a few seconds. The phase separation of colloid-polymer mixtures can take several minutes to many days. And the crystallization of the hard sphere samples can take days to weeks.

3.3.   Limitations of Testing in Aircraft

The length of time for formation of any of these structures is far too long for short term microgravity experiments, such as those performed in an airplane. For example, in the parabolic flight of the 'C-9 Low-G Flight Research' aircraft, low gravity is only achieved for less than a minute. The phase separation of colloid-polymer mixtures can take several minutes to many days. This behavior is thus too slow for either a drop tower or an airplane experiment. And the crystallization of the hard sphere samples can take days to weeks.

3.4. Need for Accommodations on the Space Station

The space station provides an environment where microgravity is sustained long enough to allow these experiments to be conducted. The samples can be homogenized by mixing them (by passing a small mix-magnet repeatedly through each sample) and then each sample can be allowed to develop under microgravity for an extended period of time without astronaut intervention in the mean time. Their structure and properties can then be probed in situ allowing the unique behavior of the new materials to be studied.

3.5. Limitations of Mathematical Modeling

Data from the BCAT-3 critical point samples indicate that the present theory for the critical behavior of atomic and molecular fluids (for which Kenneth G. Wilson was awarded the 1982 Nobel Prize) show that a direct application of the theory may not describe all of the observations we have made on ISS. When the masking effects of gravity are removed, the rate that BCAT-3 critical point samples separate into two phases show an unexpected scaling law behavior, which seems to deviate from expected (power law scaling) behavior. These experiments are essential to understand the origin of the behavior. Thus, further experiment will provide additional guidance for further refinement of the theory.

The effects of polydispersity and spherical 'seed' particles on the crystal nucleation barrier and the structure of the critical nucleus have been examined by Frenkel, *et al.* [26,27]. The recent numerical simulations make predictions concerning the structure and free energy of colloidal crystal nuclei which will be tested. Classical nucleation theory does not capture the general experimental observation that the rate of crystal nucleation passes through a maximum as the supersaturation is increased. The experimental results obtained in microgravity should be very helpful in directing future modeling and will provide the experimental input that is critical for forming and testing new models.

To date, only equilibrium simulations can accommodate sufficient numbers of particles to convincingly treat ordered systems. With non-equilibrium processes the necessity for long run times due to the slow dynamics and the importance of detailed hydrodynamic interactions have prevented progress, except for 10^1–10^2 particles in a simple shearing flow. This precludes for the foreseeable future definitive consideration of interesting problems related to the hard sphere transition, such as the nucleation and growth of the solid phase, shear induced order and shear induced melting, and the linear viscoelasticity. Most of the evidence for this transition comes from molecular dynamic studies, without viscous drag or hydrodynamic interactions, of around 10^4 particles. Results from such studies share many qualitative features with observations; the finite size of these samples leads to large regimes of supercooling and the absence of realistic hydrodynamics renders them suspect in a number of ways. Moreover, the time scale for simulations corresponds to fractions of a second in real time. Thus, there have been misleading results from early computer simulations that failed to find crystallization in high volume fraction samples. The colloidal system with around 10^{12} particles per cm^3 is truly thermodynamic with well-defined hydrodynamic and potential interactions, and is observed for macroscopic

times, thereby avoiding these problems and offering the possibility of defining the equilibrium as well as other kinetic and dynamic processes.

3.6. Limitations of Other Modeling Approaches

Other modeling is rudimentary or non-existent. The experiments proposed here will provide the definitive data that can help guide future modeling efforts.

4. Experimental Details

4.1. Experimental Samples and General Procedure to be used for BCAT-5

Brief Research Operations:
- BCAT-5 consists of ten different individual sample cells. Phase separation (PhaseSep) samples make up five of the sample cells. The remaining 5 samples (3 Compete samples, 1 SeededGrowth sample, and 1 3DMelt sample) study colloidal crystals. Please note that Compete studies both phase separation and crystallization.
- For BCAT-5-PhaseSep Samples: Crew members will homogenize these samples and photograph one sample at a time, to capture the rate of phase separation in the samples using EarthKAM automated photography over a period of 1 week – 3 weeks per sample. Images will be down-linked to allow scientists to provide immediate feedback to the astronauts.
- For BCAT-5-Compete: Crew members will homogenize the samples and photograph one sample at a time, to capture the rate of phase separation in the samples using EarthKAM automated photography over a period of days to 3 weeks per sample. Crew members will occasionally check for crystals by looking for the presence of color at various lighting angles. If crystals are found, the camera and lighting will be positioned at an angle that best captures this (the incident and scattering angles will be recorded) and the samples will be rehomogenized and a new round of photographs will be taken using EarthKAM. During these procedures, images will be down-linked to allow scientists to provide immediate feedback to the astronauts.
- For the BCAT-5-SeededGrowthand BCAT-5-3DMelt Colloidal Crystal Samples: Crew members will homogenize the samples and will look for crystals at various lighting angles. The crystals will be manually photographed and these photos down-linked allowing immediate feedback to the astronauts from the PIs. If crystals are found, the camera and lighting will be positioned at an angle that best captures this (the incident and scattering angles will be recorded) and the samples will be rehomogenized and a new round of photographs will be taken using EarthKAM. This will capture the kinetics of crystal formation.

After photography, the samples are stowed and left undisturbed to allow for the continued growth of the colloidal structure for up to 6 months.

Operational Requirements: The BCAT-5 experiment consists of ten small samples of colloidal particles contained within a small case the size of a school textbook. The experiment requires an ISS crew member to set up the experiment on the Maintenance Work Area (MWA) or on a handrail/seat track configuration, ISS Laptop and utilize EarthKAM software to take digital photographs of Samples 1 – 8 at close range using the onboard Kodak DCS760 camera. Camera Control Files for running the EarthKAM software can be uploaded from earth to control the photography intervals (how many photographs per hour) and spans (run for how many days) once it is running. Samples 6 – 10, which may form crystals, require manual photographs (at

least initially) be taken by an astronaut. The pictures are down-linked to investigators on the ground for analysis.

Operational Protocols: Sessions have slightly different photography requirements but the general operational protocol for a session is as follows:

- Crew sets up the historical Video camera to document the BCAT-5 operations as performed on-board the ISS.
- Crew sets up all hardware on MWA or ceiling rail (Slow Growth Sample Module, DCS760 Camera, pen-light source, flash and SSC Laptop with EarthKAM software.
- Crew homogenizes (mixes) the sample(s) and takes the first photographs manually. This helps them optimize the setup and shows that the samples were initially fully homogenized when publishing results later.
- EarthKAM software automates the rest of the photography session over a few days to 3-week period.
- Crew performs a Daily Status Check once a day (when time is available) to assure proper alignment and focus, and that the system is working (e.g., that a cable has not been bumped and disconnected, etc.).
- At the completion of the run, a crew member tears down and stows all hardware (30 minutes), if necessary.

4.1.1. Colloid-Polymer Critical-Point Mixtures(samples 1-5)

The materials and procedures for BCAT-5 are identical to those developed for BCAT-3 and BCAT-4. We are simply exploring samples in a slightly different position of the phase diagram. From a technical/engineering standpoint, there should be no changes needed to what already has been done and tested extensively with BCAT-3.

The colloidal particles for this experiment will again be poly(methyl methacrylate) (PMMA) particles, stabilized by a thin coating of poly(*12*-hydroxystearic acid) (PHSA), suspended in a fluid with the same index of refraction composed of *cis*-decahydronaphthalene (decalin) and *1,2,3,4*-tetrahydronaphthalene (tetralin), both hydrocarbons. The volume fractions of these samples will range from about 20.92 to 22.37 percent. The polymer will be polystyrene with an average molecular weight of 11.4 x 10^6. The colloid-polymer mixtures will be homogenized using a mixing magnet, and then photographed with a digital camera controlled by a laptop running EarthKAM software. We expect their evolution to match the features seen in BCAT-3 phase separation samples: the formation of either a bicontinuous network, or a collection of drops, that ultimately leads to complete phase separation.

4.1.2. Colloid-Polymer Three-Phase (samples 6-8)

The samples will be mixtures of PMMA particles and polymer in decalin/tetralin (similar to those described in Sec. 4.1.1). Homogenization will be performed using the standard BCAT procedure followed by imaging controlled by the EarthKAM software. The appearance of the samples will change within the first few hours or days to reveal a domain structure with interspersed crystals. Initial series of images should be recorded with a period of minutes but later images can be hours apart due to the expected slowing of the phase separation kinetics.

4.1.3. Glass phase vs. crystallization at high volume fractions (samples 9-10)

We expect colloidal crystals to form in these samples, and will use photography to study their evolution, hoping to see white light backlit samples diffract the light so that the color changes with viewing angle. This will help reveal the shape of the nuclei, which provide information about the way the crystals grow in microgravity. The crystallites might grow fast in certain crystallographic directions which could give them a layer like structure. Also their shape will give some hints about the processes that limit the growth. Comparison with analogous ground-based experiments will reveal differences in the growth behavior under microgravity.

If a crystal forms, we will place a 'mini-MagLite' flashlight (similar to the one we used in BCAT-3) behind the sample to illuminate it and see if the camera can photograph any colors that result when white light passes through a crystal and gets diffracted. If this does happen, we will then fix the camera at that position, rehomogenize the sample and use EarthKAM to watch the sample crystallize over a period of days to weeks, which is only possible in an extended microgravity environment.

Additional sample composition details are provided in Section 5.1.

4.2.   Measurements Required

4.2.1. Sample 1 – 5.

Phase Separation:
-        Homogenization by strong shearing
-        Time series of 2D color camera images

4.2.2. Samples 6-8
Three Phase Kinetics (both phase separation and crystal growth)
- Homogenization by strong shearing.
- Time series of 2D color camera images.
- Viewing samples with flashlight to check for the presence of crystals including imaging of any crystals.
- Determination of an optimum illumination angle to view and image crystals.
- Rehomogenization by strong shearing.
- Time series of 2D color camera images to record crystal formation kinetics.

4.2.2. Samples 9 – 10.

Nucleation and growth:
-        Homogenization by strong shearing
-        View samples with flashlight to see if white light is diffracted into colors that change with angle. This would indicate the presence of crystals and note where to position a camera when later recording the time evolution of these crystals.

- Measure the scattering and incident angles using the tools and procedures provided.
- Color 2D camera images to capture presence of crystals.
- Rehomogenize sample(s) and record a time series of color 2D camera images to capture the time evolution of crystal growth. This will document the rate of growth (kinetics) and position change of one or more color peaks with time.

4.3. Test Plan including Ground Characterization of Flight Hardware

We emphasize that our experiment has been designed to leverage as much pre-existing technology already resident on ISS as possible. Our only new contribution to ISS cargo will be an exact replica of the sample chamber and mixing magnet used in BCAT-3 and a simple flexible ruler attached to a cap for measuring both the angle of incidence of the illuminating light and the scattering angle where the camera is positioned. We may also substitute an updated LED Mini-Mag flashlight, which produces more light and a more uniform beam while consuming fewer batteries. All of the other pieces of our experiment, including camera, laptop computer running EarthKAM are already in orbit.

This strategy has resulted in a high level of flexibility and adaptability that has allowed a significant degree of innovation by the astronauts themselves. Even the use of EarthKAM, which increased the quality and quantity of data by more than an order of magnitude, was not suggested and implemented until we had gained several increments worth of experience with manual-only photography. We stress that astronauts Foale, Fincke, Chiao, McArthur and Williams have contributed as much as we have to the procedure currently in use, which has delivered great data to us.

We would therefore greatly benefit by having an exact replica of the entire BCAT-5 apparatus, to facilitate further development of procedures and techniques on the ground, as well as enhance communication with the astronauts actually performing our experiment. Therefore, having a complete set (sample chamber, all holders, camera, and laptop) of apparatus exactly mirroring what is currently onboard ISS would significantly increase the chance of scientific breakthroughs and the success of this experiment.

4.4. Specific Analysis Required

Major parts of the software that will be necessary for data collection and analysis exist already and are being used routinely for the data analysis of ongoing ground based experiments. In particular this includes software for image analysis and particle recognition as well as software for the recognition and structure analysis of colloidal crystals.

4.5. Preflight Experiment Planned

All experiments that are planned for BCAT-5 will also be done before the flight, either with inverted microscopes or on the flight instrument. More details about preflight experiments are given in section 4.3 above.

4.6. Post Flight Data Handling and Analysis

The same form of data analysis will be used after the flight as is used during the flight. Additional software that is required for data analysis will be purchased or written by the principal investigator team.

4.7. Mathematical Models Used

Well-accepted mathematical models representing the physics of fluid mechanics, volume fraction fluctuations, and Brownian motion will be the basis for data analysis of colloid motion in general. For the critical point samples in particular, we take the well-established theory for spinodal decomposition near the critical point as a starting basis for our analysis, recognizing that this does not seem to tell the complete story of what is happening in our colloid-polymer mixtures. We feel strongly that these experiments are meant to provide new ideas and data with which mathematical models can be constructed. Likewise, basic theories and simulations for the nucleation of spherical particles have been developed in recent years, and again we will test the applicability of these models with our experiments in BCAT-5.

4.8. Application of Results

There will be a great increase in our knowledge of the phase behavior of mixtures of colloidal particles of different types, especially for the samples that cannot be density matched. Also, new insight into the crystal structures that are formed by the high volume fraction (high ϕ) colloidal particles as well as the kinetics of their growth; the dynamics and properties of the structures formed will also be gained.

BCAT-5 has a number of applications with a large impact on the everyday life of the general public. Specifically, the colloid-polymer mixtures we study have very close analogs in a number of household products. In particular, fabric softener is composed of vesicles (which behave like colloids) and polymer, added to increase viscosity and improve product performance. The general phase behavior is of great interest to manufacturers; one of the BCAT-5 Principal Investigators is employed by Procter and Gamble (P&G), who want to add more polymer without inducing the phase separation that we are observing in the BCAT samples. They sell around US $1 billion annually, so a greater understanding of the phase behavior of these colloid-polymer mixtures will have immediate and large impact on an important household product.

Generally, the colloidal nucleation experiment seeks an understanding of the most fundamental liquid/solid transition. Though direct applications of that understanding do not drive the research, growth of ordered colloidal phases has attracted interest in a number of areas, *e.g.* ceramics, composites, optical filters and photonic bandgap materials. Moreover, there is currently great interest in using fields and gradients to control order in self-assembled systems such as diblock copolymers and microemulsions for advanced materials.

5. Experimental Requirements for BCAT-5

The following sections contain specific requirements necessary in order to fulfill the science mission for BCAT-5.

5.1. Sample Description

Colloid-polymer samples and high volume fraction (high ϕ) colloids will be used for these experiments. The PI will provide all these samples for the ground tests and flight experiments. The PI will assure sample quality, cleanliness, and suitability/compatibility for examination over the wavelength range of experimentations.

Experiment Subsystem that contains fluid (e.g. tube, bottle, syringe, etc.)	ID Label Visible to Crew (if applicable)	Chemicals/Reaction Products (including pH of acids and bases) List each component on a separate line.	Maximum Concen- tration	Maximum # of Samples	Maximum Amount Per Sample	Comments
1) Couvette, Slow Growth Sample Module	TBD	Surfactant (P&G) Polymer (CAS 26062-79-3) Calcium Chloride (CAS 10043-52-4)	1-10% wt 0.1-2.0%wt. 500ppm (in aqueous solution)	1	2.33ml	Lynch (P&G) sample
2) Couvette, Slow Growth Sample Module	TBD	Surfactant (P&G) Polymer (CAS 26062-79-3) Calcium Chloride (CAS 10043-52-4)	1-10% wt 0.1-2.0%wt. 500ppm(in aqueous solution)	1	2.33ml	Lynch (P&G) sample
3) Couvette, Slow Growth Sample Module	TBD	Surfactant (P&G) Polymer (CAS 26062-79-3) Calcium Chloride (CAS 10043-52-4)	1-10% wt 0.1-2.0%wt. 500ppm(in aqueous solution)	1	2.33ml	Lynch (P&G) sample
4) Couvette, Slow Growth Sample Module	TBD	poly(methyl methacrylate) PMMA particles with a stabilization coating of poly(hydroxystearic acid) (PHSA) Polymer Index matching solvent	Vol. fraction 22.3% wt 0.797 mg/mL 47% decalin and 53% tetralin by volume (77.63%)	1	2.33ml	Weitz-Lu (Harvard) sample
5) Couvette, Slow Growth Sample Module	TBD	poly(methyl methacrylate) PMMA particles with a stabilization coating of poly(hydroxystearic acid) (PHSA) Polymer Index matching solvent	Vol. fraction 21.73% wt 0.770 mg/mL 47% decalin and 53% tetralin by volume (78.27%)	1	2.33ml	Weitz-Lu (Harvard) sample
6) Couvette, Slow Growth Sample Module	TBD	polymethylmethacrylate (PMMA) particles with a stabilization coating of polyhydroxystearic acid (PHSA) 45% Decalin / 55% Tetralin by volume polystyrene Mw = 13.2 MDa	21% 79% 0.6 mg/ml	1	2.33ml	Frisken-Bailey (SFU) sample
7) Couvette, Slow Growth Sample Module	TBD	polymethylmethacrylate (PMMA) particles with a stabilization coating of polyhydroxystearic acid (PHSA)	26%	1	2.33ml	Frisken-Bailey (SFU) sample

		45% Decalin /55% Tetralin by volume polystyrene Mw = 13.2 MDa	74% 0.8 mg/ml			
8) Couvette, Slow Growth Sample Module	TBD	polymethylmethacrylate (PMMA) particles with a stabilization coating of polyhydroxystearic acid (PHSA) 45% Decalin / 55% Tetralin by volume polystyrene Mw = 13.2 MDa	32% 68% 0.45 mg/ml	1	2.33ml	Frisken-Bailey (SFU) sample
9) Couvette, Slow Growth Sample Module	TBD	poly(methylmethacrylate) (PMMA) spherical particles, 60% by volume particles contain a thin stabilization coating of poly(hydroxystearic acid)-g-poly(methylmethacrylate) (PHS-g-PMMA) graft copolymer refractive index matching solvent composition: 45% cis/trans decahydronaphthalene, 55% tetrahydronaphthalene (weight basis) sample volume: 1 x 2.33 mL majority particle ave. swollen diameter: 0.330 x (1.29)^0.33 = 0.360 microns (approx.) seed particles, 0.2% by weight; ave. swollen diameter: 3.80 x (1.29)^0.33 = 4.14 microns (approx.) sample class: glass, monodisperse with spherical seeds, 0.2% by weight PI sample ID: ADH012B	60% by volume 40% by volume	1	2.33ml	Chaikin-Hollingsworth (NYU) sample
10) Couvette, Slow Growth Sample Module	TBD	Poly-N-isopropylacrylamide [CAS NO. 25189-55-3]* Ammonium persulfate [CAS NO. 7727-54-0]* Methylene-bis-acrylamide [CAS NO. 110-26-9]* Water	1.9608% 0.0196% 0.0196% 98%	1	2.33ml	Yodh (U. Penn) sample

5.2. Sample Cell and Instrument Requirements

The sample cell and flight instrument shall have the capability for:

Sample Homogenization

For all samples, homogenization should be sufficient to completely mix the sample, so that there is no visible trace of any phase separation or crystallization. This usually takes about 40 passes of the mix-magnet through the sample (about 10 minutes). Homogenization shall be sufficient to "melt" the colloidal sample and disperse any existing crystallization. Homogenization must be immediately followed by photography, so that PIs can determine if homogenization is complete, as careful checking requires magnification and processing of the images (clusters of separated phases, whether liquid or crystal, are often not easily visible to the naked eye).

Optical Imaging

High magnification, visual imaging of index-matched particles with the digital SLR (Kodak DCS760 or better) is required. For the critical-point samples, the field of view must include the entire sample chamber, and should be illuminated by the camera flash. For the high ϕ colloid samples, the field of view should include the entire sample chamber, and additional photos are requested and possibly higher magnification for features (Bragg-scattering crystallites) that form in the sample. To capture these crystallites properly, additional illumination with a mini-MagLite may be required. For all samples, 3 x 12-bit RGB camera-raw images (direct data from the camera at highest resolution and bit-depth) are required, as have been delivered in BCAT-3. An f/stop setting of f/32 is preferred in order to assure the maximum depth of field, which will keep the complete depth of the sample in focus with the minimum amount of effort on the part of the astronaut.

5.3. Sample Cell Requirements

In addition to the sample cell requirements described in Section 5.2, the sample cells shall contain the colloidal samples during the length of the experiments, shall provide volumes from approximately 2 mL (*e.g.*, 10 x 20 x 0.1 mm), with rectangular shaped wells to minimize sample volume while maximizing area available for photographing. The sample cells for the critical point samples may have a larger internal dimension (if a plug is not used) because these samples are not as difficult to synthesize in volume. These sample cells shall provide for manipulation and optical viewing of the samples while being contained in a sample holder. It is also essential that each sample cell contain a stirbar, which can be moved by an external magnet to homogenize the sample volume at the beginning of an experimental. Ten sample cells are needed, with more desired.

It is absolutely crucial that the samples be loaded in a clean environment and without any formation of a visible air bubble in the sample chamber. That is, once the colloid samples are sealed in the glass cuvettes, these must be loaded into the multi-vial sample module in a clean environment, so that no dust enters before the holder is sealed.

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5.4. Delivery Requirements

For BCAT-5, it is desired that arrangements be made for <u>late delivery</u> of the samples (2 months or less before launch, preferably less). However, we will take what we can get, while understanding that <u>late stowage</u> requires much less effort for sample homogenization on the part of the astronaut.

5.5. Atmosphere Requirements

Normal pressures and temperatures of the cabin environment should suffice for the samples. For the pure solvents, the temperature should remain above freezing (greater than –40°C preferred, successfully tested to –50°C) and below boiling (< 190°C) and such that volume changes do not damage the cells (successfully tested to +50°C).

5.6. Vibration Control and Measurement

For the instrument as a whole, the dc component of gravity is most important for this work. An experiment must be long in duration, but needs no better than 10^{-3} g averaged over an hour. It is preferable that the critical-point samples not be disturbed when evolving, but this should not be viewed as a constraint that prevents measurements from being performed. In particular, short duration impulses to the ISS environment (*e.g.* from docking operations) are not expected to have any impact on these evolution processes that may take weeks or longer to occur.

If a crystallized sample is disturbed by a significantly strong impulse, its opalescence may disappear; accelerations greater than 10^{-3} could potentially disturb the ordered domains. This experiment is really more sensitive to the lower frequency accelerations. The limit on acceptable average acceleration is given by: $g_{ave} = 10^{-3}\tau^{-1/2}$, where g_{ave} is the allowable average acceleration, and τ is the time frame of interest, expressed in units of hours. Therefore, over a one hour time frame the allowable average acceleration measured at the sample cell is 1 mg (milli-g). Since the vibration environment cannot be controlled, measurement of the vibrational environment during the mission should provide enough information to determine if samples were disturbed during critical periods.

5.7. Imaging Requirements

Down-linked color images of the samples are desired just before and needed soon after homogenization. This will enable the PIs to examine the state of the samples to assess whether full homogenization has occurred before an experiment or equilibration has occurred near the end of a sample run.

In general, the BCAT-3 experiment has benefited greatly from rapid PI access to all of the raw data as very soon after it is collected in-flight. We have had great success with the Digital Imagery Management System (DIMS) Exchange system, allowing the PIs to access and analyze data soon after it is taken on orbit. With rapid communication back to the astronauts, in many cases, we have been able to make significant improvements to our

data taking and analysis because of this direct communication. It is therefore crucial to have access to as much data as soon as possible while the experiment is progressing.

5.8.   Astronaut Involvement

Astronaut involvement is envisioned for setting up the experiment to be photographed.

On-Orbit Operations and Crew Time Estimate

Sample number	Session number	Run time (days)
1	1	13
2	1	13
3	1	13
4	1	13
5	1	13
6	2	21
7	2	21
8	2	21
9	3	21
10	4	21
1– 10	5	Mix (dependent upon crystal formation) and photograph samples
1– 10	6	6-month sample photos

Note: On May 7, 2008 it was decided to add a new procedure for the crystal samples (keeping the original Daily Status Check procedure for the Phase Separation samples) where the Daily Status Check will be modified to include additional steps to look for crystals, call down the color and approximate angle then ultimately make the measurements to determine the scattering angle.

Session 1 **(Homogenize and Photograph Samples 1, 2, 3, 4 and 5 for 13 days each; 65 Days Total)**
(Extra setup and tear-down times must be added if not running all 5 samples consecutively)

Crew FAM	15 minutes
Historical Video Set-Up	10 minutes
Set up all hardware	60 minutes
P/TV Still Photos (any time during homogenization	

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and/or photography of sample of choice)	10 minutes
Homogenize Sample **1**, take first photographs manually	30 minutes
Photograph Sample **1** automatically for 13 days	
Daily Status Checks (12 days x 5 minutes)	60 minutes
Homogenize Sample **2**, take first photographs manually	30 minutes
Photograph Sample **2** automatically for 13 days	
Daily Status Checks (12 days x 5 minutes)	60 minutes
Homogenize Sample **3**, take first photographs manually	30 minutes
Photograph Sample **3** automatically for 13 days	
Daily Status Checks (12 days x 5 minutes)	60 minutes
Homogenize Sample **4**, take first photographs manually	30 minutes
Photograph Sample **4** automatically for 13 days	
Daily Status Checks (12 days x 5 minutes)	60 minutes
Homogenize Sample **5**, take first photographs manually	30 minutes
Photograph Sample **5** automatically for 13 days	
Daily Status Checks [DSC] (12 days x 5 minutes)	60 minutes
Tear down/stow all hardware	30 minutes
TOTAL	**9 hours 35 minutes**

Session 2 **(Homogenize and Photograph Samples 6, 7 and 8 for 20 days each; 60 Days Total)**
(Extra setup and tear-down times must be added if not running all 3 samples consecutively)

Crew FAM	15 minutes
Historical Video Set-Up	10 minutes
Set up all hardware	60 minutes
P/TV Still Photos (any time during homogenization	
and/or photography of sample of choice)	10 minutes
Homogenize Sample **6**, take first photographs manually	30 minutes
Photograph Sample **6** automatically for 10 days:	
Sample **6** Daily Status Checks (10 days x 5 minutes)	50 minutes
Perform crystal check using MML, view through camera	30 minutes
(keeping camera stationary)	
-if crystals found, call down the brightest peak color,	
approximate angle of flash to sample module	
-move flash into MML's position, take a test photo,	
repeat to capture peak color in test photos	
Homogenize Sample **6**, take first photographs	

manually without repositioning camera	15 minutes
Photograph Sample **6** automatically for 10 days:	
Sample **6** Daily Status Checks (10 days x 5 minutes)	50 minutes
Homogenize Sample **7**, take first photographs manually	30 minutes
Photograph Sample **7** automatically for 10 days:	
Sample **7** Daily Status Checks (10 days x 5 minutes)	50 minutes
Perform crystal check using MML, view through camera	30 minutes

      (keeping camera stationary)
      -if crystals found, call down the brightest peak color,
      approximate angle of flash to sample module
      -move flash into MML's position, take a test photo,
      repeat to capture peak color in test photos

Homogenize Sample **7**, take first photographs manually without repositioning camera/flash	15 minutes
Photograph Sample **7** automatically for 10 days:	
Sample **7** Daily Status Checks (10 days x 5 minutes)	50 minutes
Homogenize Sample **8**, take first photographs manually	30 minutes
Photograph Sample **8** automatically for 10 days:	
Sample **8** Daily Status Checks (10 days x 5 minutes)	50 minutes
Perform crystal check using MML, view through camera	30 minutes

      (keeping camera stationary)
      -if crystals found, call down the brightest peak color,
      approximate angle of flash to sample module
      -move flash into MML's position, take a test photo,
      repeat to capture peak color in test photos

Homogenize Sample **8**, take first photographs manually without repositioning camera/flash	15 minutes
Photograph Sample **8** automatically for 10 days:	
Sample **8** Daily Status Checks (10 days x 5 minutes)	50 minutes
<u>Tear down/stow all hardware</u>	<u>30 minutes</u>
TOTAL	**10 hour 50 minutes**

Session 3 **(Homogenize and Photograph Sample 9 for 21 days; 21 Days Total)**
(Extra setup and tear-down times must be added if not running all 3 samples consecutively)

Crew FAM	15 minutes
Historical Video Set-Up	10 minutes
Set up all hardware	60 minutes
P/TV Still Photos (any time during homogenization	

and/or photography of sample of choice)   10 minutes

**Homogenize Sample 9, take first photographs
manually**   **30 minutes**

Photograph Sample 9 automatically for 21 days:
Sample **9** Daily Status Checks (20 days x 5 or 10 minutes)
(Some DSCs may be increased to 10 minutes while
        capturing, photographing and/or making
         measurements)   *100-200 minutes*
Daily Status Check procedure will be modified to include:
        -crystal checks using MML, view through camera
        (keeping camera stationary)
        -if crystals found, call down the brightest peak color,
        approximate angle of flash to sample module
        -move flash into MML's position, take a test photo,
        repeat to capture peak color in test photos
*Upon examination of the following automated photos, we will determine whether to
repeat these steps during the next DSC (peak color not captured) or let it run (peak color
captured).*
*If letting it run, perform the 8 (4?) measurements during a future DSC (preferably a DSC
later in the run or on the last day if the photos are really good to decrease the chance of
moving the camera)*

Session 4 **(Homogenize and Photograph Sample 10 for 21 Days; 21 Days Total)**
(Extra setup and tear-down times must be added if not running all 3 samples
consecutively)

Crew FAM   15 minutes
Historical Video Set-Up   10 minutes
Set up all hardware   60 minutes
P/TV Still Photos (any time during homogenization
and/or photography of sample of choice)   10 minutes

**Homogenize Sample 10, take first photographs
manually**   **30 minutes**

Photograph Sample 10 automatically for 21 days:
Sample **10** Daily Status Checks (20 days x 5 or 10 minutes)
(Some DSCs may be increased to 10 minutes while
        capturing, photographing and/or making
         measurements)   *100-200 minutes*
Daily Status Check procedure will be modified to include:
        -crystal checks using MML, view through camera

(keeping camera stationary)
-if crystals found, call down the brightest peak color,
approximate angle of flash to sample module
-move flash into MML's position, take a test photo,
repeat to capture peak color in test photos

Upon examination of the following automated photos, we will determine whether to repeat these steps during the next DSC (peak color not captured) or let it run (peak color captured).

If letting it run, perform the 8 (4?) measurements during a future DSC (preferably a DSC later in the run or on the last day if the photos are really good to decrease the chance of moving the camera)

Session 5 (Photograph Samples 1 – 10 after all previous ops are completed):

Crew FAM	15 minutes
Historical Video Set-Up	10 minutes
Set up all hardware	60 minutes
Photograph Samples 1– 10	50 minutes
Tear down/stow all hardware	30 minutes
TOTAL	2 hours 45 minutes

Session 6 (Photograph Samples 1 – 10 after they have equilibrated for 6 months):

Crew FAM	15 minutes
Historical Video Set-Up	10 minutes
Set up all hardware	60 minutes
Photograph Samples 1– 10	50 minutes
Tear down/stow all hardware	30 minutes
TOTAL	2 hours 45 minutes

Please note that all the photos are downlinked through EarthKAM, even when the photos are taken manually by the astronauts. Therefore, no astronaut time is required for downlinking photos.

5.9.   Data Requirements

On-board data storage requirements:

- All visual images, and other such data should be time-tagged to MET, and GMT.
- Voice annotation of photographs is desired when deemed appropriate by the astronaut.
- Accelerations in excess of 10^{-3} g should be recorded and time-tagged for comparison with data from the experiment.

- All images should be stored with a record of the experimental conditions such as, when the measurement was made, length of measurement, if and how lighting conditions have changed.
- Where possible, temperature should to be recorded whenever photographs are taken, especially for Sample 10, where temperature drives the science being studied (by causing melting and crystallization). Simple cabin temperature measurements in the area of the experiment will suffice.
- Visual images of samples are desired just before and after homogenization (5.2.1) and periodically (see Science Requirements Summary Table that follows).
- Need capability to periodically downlink any of the above data.

Science Requirements Summary Table

Parameter	Section	Requirement
5.9.1 Samples (compositions)	5.1, 4.1	• PHSA-coated monodisperse PMMA particles in an index matching mixture of decalin and tetralin, with and without linear polystyrene particles, with the addtions stated in Section 5.1. • Particle sizes: diameters between 100 and 500 nm. • Index of refraction: 1.511 at the sodium D line at 20 °C • Volume fractions: $0.2 < \phi < 0.74$
5.9.2 Sample mixing	5.2.1	• Homogenize samples at beginning of each experiment run (one sample at a time preferred, but not essential).
5.9.3 Optical imaging (visual camera images)	5.2.2 4.2.1, 4.2.2	• High magnification, color visual images of colloidal particles; nominally 0.01–5.0µm in size and refractive index matched (to 0.001). • Field of view to include the full length of the sample cells, with additional magnified photographs taken of portions of the sample the astronaut deems interesting (*e.g.*, dendrites, crystals, droplets). • Images should be taken at maximum camera resolution and bit-depth, and down-linked in the camera-raw (unprocessed) format. • Resolution depth up to 90 µm into a sample of 0.1 optical density; up to 100 µm into the sample is desired. • Record videos at: 30 Hz • Capability for some near real time downlink of video and still images to assist with homogenization (5.2.1) and planning of additional experiment runs. • Note that the capabilities that would be needed for imaging the sample types are: 2K x 3 K resolution, as provided by the Kodak DCS760 (or better) camera with a 105 mm focal length lens and the camera set at f/32 (as in BCAT-3).

Parameter	Section	Requirement
Timing of camera images	5.2.2 5.8	• Photographs are to be taken immediately after mixing, then hourly, or every several hours, controlled by EarthKAM software. • Minimum photography requirements: 10 samples x 3 photos per sample = 30 photos per photo session x 4 = 120 photos after 1 day; then 30 x 3 = 90 photos more for a minimum of 210 photos total; plus a repeat (= 420 photos) and hopefully more in between ... say 500 photos.
Wavelength range and respective incident angle range of light source at the sample	5.2.2	• A flight-qualified mini-MagLite flashlight is sufficient for an illumination source for manually taken photos. And the camera flash with its autoexposure capability is ideal when using EarthKAM. The light focus should be adjusted by rotating the lens cap on the flashlight under the light is approximately collimated. This can be verified by moving the flashlight toward and away from a wall and adjusting the lens cap until the spot-size remains approximately constant. The wavelength of the source is fine in the range of 400–700 nm. The angular range should be continuously adjustable to roughly 2.0 degrees resolution in the *x-z* or *y-z* planes. There is no coherence length requirement or polarization requirement for the illuminating light source.
Illumination level at the sample	5.2.2	• Intensity of source light (I_0) will be fixed by the inherent flashlight output. This does not need to be modified unless the batteries are low and need changed. Continuous illumination (or flash illumination once the optimum camera position has been selected) during photography of Samples 9–10 (and possibly 6–8 if they crystallize) is desirable for setup and for finding crystals. Flash backlighting (when samples are not opaque and using the flash for lighting on the same side as the camera when the samples are opaque or exhibit large amounts of multiple scattering) with automatic exposure, once the camera position has been set, of Samples 1–10 is desirable.
Angle precision and	5.2.2	• The angle at which the most detailed images of any structure (if existent) in a

repeatability		sample cell is visible. This may be in either the forward or backscatter direction. Sample opacity may limit this for samples 1–5, but if possible, we will attempt to engineer the samples so that they can be photographed using forward scattering. Sample 10 is likely to exhibit opacity and hence require lighting from the camera side of the sample when being photographed.
Camera (or other detector)	5.2.2	• Kodak 760 (or better) camera with a 105-mm focal length lens and the camera set at f/32 (as in the later BCAT-3 flight experiments). Images stored on EarthKAM for downlinking capability.

Parameter	Section	Requirement
5.9.4 Sample cell requirements	5.3	• Provide adequate containment of the colloidal samples during the length of the experiments. • Sample cell volumes of 2 mL (possibly more for the critical fluids if the plug is removed). • 10 sample cells are needed. • Sample cells must be loaded so that no visible air bubble is present in the samples. A bubble may form from cavitation and will likely move into the non-wetting Teflon plug. • A Teflon coated mixing magnet is inside of each cuvette to allow for homogenization.
5.9.5 Atmospheric requirements	5.5	• Normal cabin pressure and temperature environment is sufficient.
5.9.6 Vibration control & measurement	5.6	• Averaged over an hour, needs no better than 10^{-3} g of dc g-level; especially after homogenization and prior to measurements, avoid jarring disturbances.
5.9.7 Access to image requirements	5.7	• Downlinked color CCD images of the samples are needed just before and after homogenization, and at various stages during crystallization/phase separation.
5.9.8 Astronaut involvement	5.8	• Significant during sample homogenization and photography. Approximately 25 incremental hours are required (when available).
5.9.9 Data requirements	5.9	• All visual images, and other such data should be time-tagged to MET, and GMT. • Accelerations in excess of 10^{-3} g should be recorded and time-tagged for comparison with data from the experiment if SAMS is running and already available. • All images should be stored with a record of the experimental conditions such as, when the measurement was made, beam and detector positions (forward- or back-illumination measurement, temperature, and any off-nominal conditions (astronaut exercising on bicycle during photography, etc.). • Visual images of samples are desired just before and are required soon after homogenization (5.2.1) and periodically. • Need capability to periodically downlink any of the above data.

5.10. Postflight Data Deliverables

- All CCD sample pictures and associated metadata with timestamps and voice annotations of interesting features.
- History of various setting, such as, camera settings (and a note of when and what changes occur in these settings).
- SAMS data if readily available (gravitational acceleration monitoring) in a useful format (*e.g.*, a graphical plot instead of CDs of acceleration data would help us in making use of acceleration information).
- <u>Immediate access</u> to samples: all samples (if available), for further studies at the PI labs, <u>as soon as samples return from orbit</u>, or as soon as possible. It is the glassy volume fraction PMMA samples that are likely to survive the accelerations of a space shuttle reentry. By homogenizing either the top or bottom half of the sample and letting it stand, it can be clearly demonstrated that the same sample crystallized in microgravity and not on earth, even with a crystallized surface to initiate crystallization. Not only is such a sample of scientific significance, but the results of this very significant demonstration should be sent to a museum.

5.11. Mission Success Criteria for BCAT-5

Complete success is the achievement of all of the science requirements. This means that there will be sufficient information to provide a crosscheck of all data and calculated factors.

Processing, manipulation and characterization of the samples in microgravity are as important as the measurements during the experiments themselves. For example, sample homogenization is essential to conduct of any of the flight experiments. This allows for the dissolution of the crystallites or structures that have formed in 1-g before launch, and provides a proper starting point in microgravity.

Success Level	Accomplishment
Minimum Success	• Homogenize and photograph all of the ten samples at least twice (Req.5.1) – all the high ϕ colloidal particle samples and all the colloidal phase separation samples. This includes a photograph of each sample right after is has been homogenized to ensure this is indeed the case and another photograph several weeks or more later to capture the equilibrium state of the sample.
Significant Success	• Homogenize and photograph all ten samples for at least one homogenization photo and three photo sessions (Req.5.1) – all the high ϕ colloidal particle samples and all the colloidal phase separation samples.

Complete Success	• Homogenize and photograph all ten samples using EarthKAM to capture the kinetics (time evolution) of the samples (Req.5.1) – all the high ϕ colloidal particle samples and all the colloidal phase separation samples. The samples should be returned to earth if any of the concentrated ("glassy") samples crystallize since these crystals will likely survive re-entry.

6. Test Matrix

The current plan for this experiment is to conduct it over five, three-week sessions, each of each can be run incrementally and will require 4 to 5 hours of crew-time; and a sixth session at six months, which is slotted to take about an hour of crew-time. As such, new information will undoubtedly be learned, and the nature of the experiments conducted will evolve to take advantage of this new information. As a result, it is essential to allow the PIs as much flexibility with the experiment as possible. The test matrices should be viewed as representative of the sort of experiments that will be conducted and can be found in detail in Section 5.8, which is titled "Astronaut Involvement".

7. Principal Investigators' Requests

7.1.Research Equipment

Preflight

We would greatly benefit by having an exact replica of the entire BCAT-5 apparatus to facilitate further development of procedures and techniques on the ground and to enhance communication with the astronauts actually performing our experiment. Therefore, having a complete set (sample chamber, all holders, camera, and laptop) of apparatus for the duration of the experiment exactly mirroring what is currently onboard ISS would significantly increase the chance of scientific breakthroughs and the success of this experiment.

Because the development of our experiment has benefited greatly from the use of tools primarily proposed for other uses onboard the ISS, we would also like to have a list of the available equipment (*i.e.*, not critical components that cannot be moved) that might be potentially used to assist our experiment. For instance, the use of the EarthKAM system has radically improved the quantity and quality of our data. We expect that further improvements could be conceived, and thus would appreciate a list of accessible equipment.

Postflight

Optional access to the flight samples and a functional engineering model of the equipment could allow some of the observations to be tested, and the conditions to be repeated on the ground. This may prove important in interpretation of the data obtained.

8. References

1.   P.N. Pusey and W. van Megen, *Nature (London)* **320** 340 (1986).
2.   M.D. Eldridge, P.A. Madden and D. Frenkel, *Mol. Phys.* **79** 105 (1993).
3.   M.D. Eldridge, P.A. Madden and D. Frenkel, *Nature (London)* **365** 644 (1993).
4.   M.D. Eldridge, P.A. Madden and D. Frenkel, *Mol. Phys.* **80** 987 (1993).
5.   M.D. Eldridge, P.A. Madden, P.N. Pusey and P. Bartlett, *Mol. Phys.* **84** 395 (1995).
6.   S. John, *Phys. Rev. Lett.* **58** 2486 (1987).
7.   E. Yablanovitch, *Phys. Rev. Lett.* **58** 2059 (1987).
8.   J. Martorell and N.M. Lawandy, *Phys. Rev. Lett.* **66** 887 (1991).
9.   H.N.W. Lekkerkerker, W.C.-K. Poon, P.N. Pusey, A. Stroobants and P.B. Warren, *Europhys. Lett.* **20** 559 (1992).
10.   W.C.K. Poon, J.S. Selfe, M.B. Robertson, S.M. Ilett, A.D. Pirie and P.N. Pusey, *J. Phys. (France) II* (1994).
11.   S.M. Ilett, A. Orrock, W.C.K. Poon and P.N. Pusey, *Phys. Rev.* **E51**, 1344 (1995).

12. F.L. Calderon, J. Bibette and J. Biais, *Europhys. Lett.* **23** 653 (1993).
13. P.N. Pusey, W. van Megan, P. Bartlett, B.J. Ackerson, J.G. Rarity and S.M. Underwood, *Phys. Rev. Lett.* **63** 2753 (1989).
14. T. Alfrey, E.B. Bradford, J.W. Vanderhoff and G. Oster, *J. Opt. Soc. Am.* **44** 603 (1954).
15. P. Pieranski, *Contemp. Phys.* **24** 25 (1983).
16. P. Bartlett, R.H. Ottewill and P.N. Pusey, *J. Chem. Phys.* **93** 1299 (1990).
17. P. Bartlett, R.H. Ottewill and P.N. Pusey, *Phys. Rev. Lett.* **68** 3801 (1992).
18. J. Bibette, D. Roux and F. Nallet, *Phys. Rev. Lett.* **65** 2470 (1990).
19. D. Weaire and R. Phelan, *Philisophical Magazine Letters* **69** 107 (1994).
20. W.C.K. Poon, A.D. Pirie and P.N. Pusey, *Faraday Discuss.* **101** 65–76 (1995).
21. P.N. Pusey and W. van Megen, *Physica A* **157** 705 (1989).
22. A.H. Krall and D.A. Weitz, *Phys. Rev. Lett.* **80** 778 (1998).
23. A. van Blaaderen and P. Wiltzius, *Science* **270**, 1177–1179 (1995).
24. A. van Blaaderen, R. Ruel and P. Wiltzius, *Nature* **385** 321–324 (1997).
25. P.N. Segrè, V. Prasad, A. B. Schofield, and D. A. Weitz, *Phys. Rev. Lett.* **86** 6042–6045 (2001).
26. S. Auer, D. Frenkel *Nature* **413** 711 (2001).
27. A. Cacciuto, S. Auer, D. Frenkel *Nature* **428** 404 (2004)

Several publications are in preparation for submission to peer-reviewed journals.

Related Publications:

Samples 1 – 5 (Lynch, Weitz, and Lu)

Peter J. Lu, Emanuela Zaccarelli, Fabio Ciulla, Andrew B. Schofield, Francesco Sciortino and David A. Weitz. "Gelation of particles with short-range attraction," _Nature_ doi:10.1038/nature06931, (2008).

Huh, Lynch, Furst. Microscopic structure and collapse of depletion-induced gels in vesicle-polymer mixtures Phys. Rev. E 76, 051409 (2007).

A.E. Bailey, W.C.K. Poon, R.J. Christianson, A.B. Scholfield, U. Gasser, V. Prasad, S. Manley, P.N. Segre, L. Cipelletti, W.V. Meyer, M.P. Doherty, S. Sankaran, A.L. Jankovsky, W.L. Shiley, J.P. Bowen, J.C. Eggers, C. Kurta, T. Lorik, Jr., P.N. Pusey, and D.A. Weitz, "Spinodal Decomposition in a Model Colloid-Polymer Mixture in Microgravity," PRL 99, 205701, Nov. 16, 2007.

Lu PJ, Weitz DA, Foale CM, Fincke EM, Chiao L, McArthur WS, Williams JN, Meyer WV, Owens J Hoffmann MI, Sicker RJ, Rogers RB, Frey CA, Krauss AS, Funk GP, Havenhill MA, Anzalone SM, and Yee HL, Science Applications International Corporation, Microgravity Phase Separation Near the Critical Point in Attractive Colloids, Proceedings of the 45th Aerospace Sciences Meeting and Exhibit. 2007; AIAA-2007-1152.

Gopalakrishnan V, Schweizer KS, Zukoski CF, Linking single particle rearrangements to delayed collapse times in transient depletion gels, JOURNAL OF PHYSICS-CONDENSED MATTER 18 (50): 11531-11550, DEC 20 2006.

Manley S, Skotheim JM, Mahadevan L, *et al.*, Gravitational collapse of colloidal gels, PHYSICAL REVIEW LETTERS 94 (21): Art. No. 218302 JUN 3 2005.

Blijdenstein TBJ, van der Linden E, van Vliet T, *et al.*, Scaling behavior of delayed demixing, rheology, and microstructure of emulsions flocculated by depletion and bridging, LANGMUIR 20 (26): 11321-11328, DEC 21 2004.

Verhaegh NAM, Asnaghi D, Lekkerkerker HNW, *et al.*, Transient gelation by spinodal decomposition in colloid-polymer mixtures, PHYSICA A 242 (1-2): 104-118 AUG. 1 1997.

Samples 6 – 8 (Frisken and Bailey):

Z. Cheng, J. Zhu, W. B. Russel, W.V. Meyer and P. M. Chaikin, Applied Optics 40, 4146 (2001).

Z. Cheng, P. M. Chaikin, J. Zhu, W.B. Russel and W.V. Meyer, Phys. Rev. Lett. 88, 015501 (2001).

W.B. Russel, P.M. Chaikin, J. Zhu, W.V. Meyer and R. Rodgers, Langmuir 13, 3871 (1997), J. Zhu, M. Li, R. Rogers, W. Meyer, R. H. Ottewill, STS-73 Space Shuttle Crew, W. B. Russel, and P. M. Chaikin, Nature 387, 883 (1997).

E.H.A. de Hoog, W.K. Kegel, A. van Blaaderen and H.N.W. Lekkerkerker, Phys. Rev. E. 64, 021407 (2001).

Sample 9 (Chaikin and Hollingsworth):

"Experiments on Random Packings of Ellipsoids", Man WN, Donev A, Stillinger FH, Sullivan MT, Russel WB, Heeger D, Inati S, Torquato S, Chaikin PM, Phys. Rev. Lett. 94, 198001 (2005).

"Unusually Dense Crystal Packings of Ellipsoids", Aleksandar Donev, Frank H. Stillinger, P. M. Chaikin, and Salvatore Torquato, Phys. Rev. Lett. 92, 255506-1 (2004).

"Improving the Density of Jammed Disordered Packings Using Ellipsoids," Aleksandar Donev, Ibrahim Cisse, David Sachs, Evan A. Variano, Frank H. Stillinger, Robert Connelly, Salvatore Torquato, and P.M. Chaikin, Science 303, 990-993 (2004).

Sample 10 (Yodh):

M. F. Islam, M. Nobili, Fangfu Ye, T. C. Lubensky, and A. G. Yodh, Cracks and Topological Defects in Lyotropic Nematic Gels, *Physical Review Letters* 95, 148301 (2005).

Alsayed, A.M., Islam, M.F., Zhang, J., Collings, P.J., Yodh, A.G., Premelting at defects within bulk colloidal crystals. *Science* 309, 1207-1210, (2005).

Alsayed, A.M., Dogic, Z., and Yodh, A.G., Melting of lamellar phases in temperature sensitive colloid-polymer suspensions. *Physical Review Letters* 93, 057801-1-057801-4 (2004).

Islam, M.F., Alsayed, A.M., Dogic, Z., Zhang, J., Lubensky, T.C., and Yodh, A.G., Nematic nanotube gels. *Physical Review Letters* 92, 088303-1-088303-4 (2004).

Media Coverage:

- GLT Science "Uncommon Knowledge", http://wglt.org/programs/uncommon/index.phtml, Why are Colloids Important? (USA, 5 February 2007) [mp3]

- NASA ISS Payloads Newsletter (USA, September 2004) [pdf]

- [Science@NASA](#) (USA, 16 June 2004)

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